BIOPETROL SYNTHESIZED FROM OLEIC ACID – HETEROGENOUS CATALYTIC CRACKING BY USING GRANULAR METAL AS CATALYST

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ABSTRACT

Current petrol disaster and valuable oleic acid loss by disposal to environment are the reason why that biopetrol should be synthesized from oleic acid. Biopetrol is defined as liquid or gas that can be produced from natural vegetable oil or fat which has the same characteristic with commercial petrol in terms of its molecular structure. Oil palm is widely grown in Malaysia, palm oil has attracted the attention of researcher to develop an environmental friendly and high quality fuel, free from nitrogen and sulfur. The objective of this study is to determine concentration of synthesized biopetrol (dominated by isooctane) obtained. Catalytic cracking process is used to synthesize isooctane, using cooper as catalyst. Oleic acid is naturally in liquid form, so oleic acid is directly heated in the range of temperature 90^{o} C-100^{o} C for 2 hours in order to obtain isooctane, with catalyst is in moving form. Various rotation speeds are used in this study which is 600 rpm, 700 rpm, 850 rpm and 1000 rpm. The sample will be analyzing with Gas Chromatography (GC) with the Fire Ionization Detector method (FID). The sample will be compare with the retention time of standard calibration of pure isooctane in order to determine the actual concentration of isooctane in sample. The desired isooctane obtain is around 0.04201% - 0.16302% in the distilled oleic acid, with the presence of hexane as dilution solvent. After applying back calculation to obtain actual concentration the highest concentration of desired isooctane in oleic acid distillate is 44.94% at 700 rpm.

ABSTRAK

Harga petrol yang tidak menentu dan kerugian oleh pembuagan asid oleic ke persekitaran adalah alasan mengapa biopetrol yang harus disintesis daripada oleic asid. Biopetrol ditakrifkan sebagai cecair atau gas yang boleh dihasilkan dari minyak tumbuhan atau lemak haiwan yang mana ia mempunyai ciri-ciri yang sama dengan petrol komersil dari segi struktur molekulnya. Kelapa sawit banyak ditanam di Malaysia, minyak sawit telah menarik perhatian penyelidik untuk membangunkan bahan bakar yg mesra alam dan tinggi kualiti, bebas dari nitrogen dan sulfur. Tujuan kajian ini adalah untuk menentukan kepekatan biopetrol disintesis (didominasi oleh isooctane) yang diperoleh. Cracking katalitik proses digunakan untuk mensintesis isooktana, dengan menggunakan tembaga sebagai mangkin. Asid oleik secara semulajadi dalam bentuk cecair, jadi oleik asid dipanaskan didalam lingkungan suhu 90^{O} C-100^{O} C selama 2 jam untuk mendapatkan isooktana, dengan mangkin dalam bentuk bergerak. Pelbagai kelajuan digunakan di dalam kajian ini antaranya 600rpm, 750rpm, 850rpm, dan 1000 rpm *(*Pusingan per minit). Contoh kajian diuji dengan menggunakan Gas Chromatography (GC) dengan pengesan pengionan api (FID). sampel ini akan dibandingkan dengan waktu retensi standard kalibrasi isooktana untuk menentukan kepekatan sebenar isooktana dalam sampel. Isooktana dikehendaki mendapatkan sekitar 0.04201% - 0.16302% dalam asid oleik suling, dengan kehadiran pelarut Heksan pengcernaan. Setelah melaksanakan pengiraan semula untuk mendapatkan kepekatan yang sebenarnya kepekatan tertinggi isooktana dikehendaki dalam distilat asid oleik adalah 44.94% pada 700 rpm (Pusingan per minit).

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P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
n	-	Number of moles
L	-	Liter

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CHAPTER 1

INTRODUCTION

1.0 Introduction

In this part the background of study, problem statement, research objectives, and significance of study will be overlooked. This is a study on biopetrol synthesized from oleic acid- heterogeneous catalytic cracking.

1.1 Background of Study

Petrol or commonly known as gasoline that is used today is a complex mixture of hydrocarbon. Petroleum like gas and coal is a fossil fuel formed in the geologic past, this fuels is a finite resource. With the unstable price of fossil oil and limited supply of crude oil, Biopetrol is an alternative fuel similar to conventional or ‘fossil’ petrol. Technology today grows rapidly whereby people can depend on other sources such as Biofuel and Biodiesel to encounter the limited supply of petroleum. Biopetrol can be produced from straight vegetable oil, animal oil, tallow and waste cooking oil. Plant oil has recently got attention due to the environmental benefits and renewable source. They have potential to substitute for the petroleum fuels in future (Demirbas, 2003).

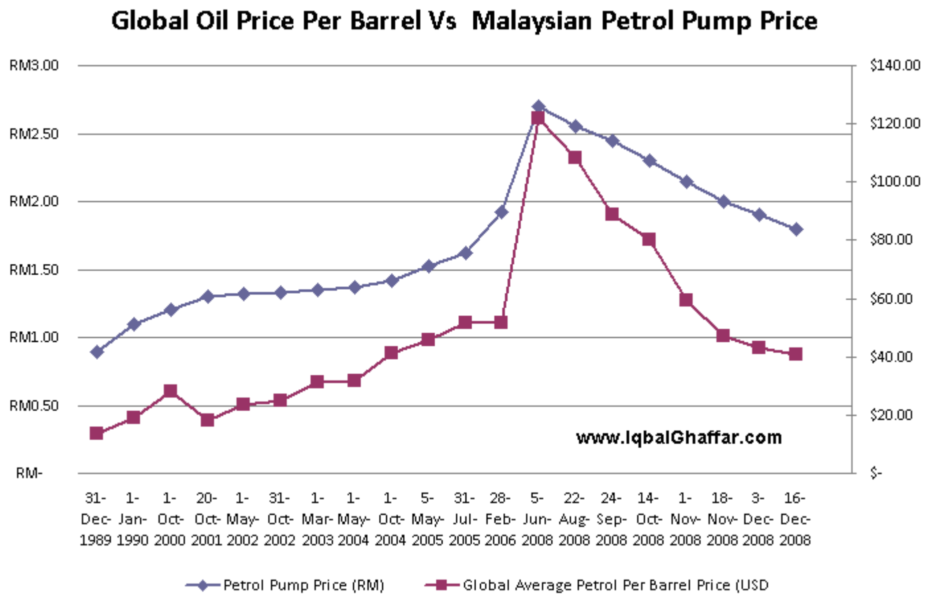

Figure 1.1: Global Oil Price Per Barrel Vs Malaysian Petrol Pump Price

The price of fossil fuels nowadays is increasing drastically that caused many others expense to increase. From figure 1.1, the blue line represent petrol pump price (RM). The figure shows that the highest price of petrol is on July 2007 which is RM 2.70 L^{-1} before it decreasing to RM 1.80 L^{-1} on March 2008, and now the price of fuel is RM 1.80 L^{-1} for RON 95 and RM 2.10 L^{-1} for RON 97. However, that price is still high.

1.2 Problem Statement

Environmental pollution, limited supply of fossil fuels and increasing of global crude oil price is the main keys that lead to search for other alternatives way in other to sustain energy supply for transportation. Other problem regarding this matter is that:

- Petrol is much more consumed than diesel
- Current biodiesel production is limited for biodiesel-used vehicle only
- Food and biofuel industries use same crude vegetable oil, so they compete each other.

- Fatty acids (e.g. oleic acid) in crude vegetable oil are always being eliminated instead of utilizing them, and disposed as palm oil waste into water supply.

Biopetrol from oleic acid is believe to be a potential to reduce the emission of greenhouse emitted by the fossil fuel such as carbon dioxide (CO2), sulphur dioxide (SO2) and carbon monoxide (CO). Biofuel as a buffer to greenhouse gas emission is proved by the success of the emission reduction of rapeseed-derived biodiesel range 40% -60% compared to convectional diesel fuel in light-duty compression ignition engines 216 page IEA report (p.63)(Shelley,2008).

1.3 Objectives

i. To find and determine concentration of synthesized biopetrol obtained
ii. To synthesize biopetrol as alternative fuel for petrol-used vehicles from fatty acids

1.4 Rationale and Significance

i. Biopetrol is biodegradable and renewable resource, able to sustain the energy supply for transportation.
ii. Oleic acid can be found easily in most vegetable oil especially in palm oil (Malaysia) and wider the palm oil application for biopetrol.
iii. Isooctane (B100) obtain in biopetrol by catalytic cracking reduce the hydrocarbon chain cause effective combustion in petrol engine and increase engine life
iv. Catalytic cracking provide higher conversion of hydrocarbon than thermal cracking does by lowering the activation energy of the reaction

1.5 Scopes of Study

In order to accomplish the objectives, the scope of this research is focusing on the criteria that are stated as below:-

i. Conversion of fatty acid to form desired isooctane in biopetrol through catalytic cracking.
ii. Selection of various rotation speeds for performing catalytic cracking method applied to the fatty acids.
iii. Qualitative and quantitative analysis of biopetrol through gas chromatography analysis using mixture of hexane and pure isooctane as standard calibration

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

Petroleum is a complex mixture of hydrocarbon with various molecular weights and also consists of other organic compound which can be found in rock, formation of Earth. Petrol or commonly known as gasoline is obtained from refinement of crude oil and widely used in many application today. Because of limited supply of crude oil, biopetrol would be the alternative way to slow down the rate of producing gasoline. Biopetrol is environmental friendly and cost of production is less expensive than gasoline.

Previous studies by European Union and British Enviromental Ministry, biopetrol process based on agriculture oil as raw material and it have only minor effect on the prices. There are 2 types of engine that apply on vehicle which is diesel engine and gasoline engine. Biodiesel only suitable for diesel engine, bioethanol is the new technologies that apply the principle of fuel as petrol. Isooctane is the major component of gasoline, therefore development of producing bio-gasoline in needed for fuel transport vehicle. Catalytic cracking method will be used to break hydrocarbon chain in oleic acid to produce isooctane by using copper as catalyst

2.1 Fuel Types by Period of Natural Renovation

2.1.1 Fossil Fuel

Fossil fuels formed by natural resources such as anaerobic decomposition of buried dead organism. The age of the organisms and their resulting fossil fuel is typically millions of years, and sometimes exceeds 650 million years. These fuels contain a high percentage of carbon and hydrocarbons. Fossil fuels are non-renewable resources because they take millions of years to form, and reserves are being depleted much faster than new ones are being formed. The production and use of fossil fuels raise environmental concerns. A global movement toward the generation of renewable energy is therefore under way to help meet increased energy needs. There is a wide range of organic, or hydrocarbon, compounds in any given fuel mixture. The specific mixture of hydrocarbons gives a fuel its characteristic properties, such as boiling point, melting point, density, viscosity, etc. Some fuels like natural gas, for instance, contain only very low boiling, gaseous components. Others such as gasoline or diesel contain much higher boiling components.

Fossil fuels importance because they can be burned (oxidized to carbon dioxide and water), producing significant amounts of energy. The use of coal as a fuel predates recorded history. Coal was used to run furnaces for the melting of metal ore. Semi-solid hydrocarbons from seeps were also burned in ancient times, but these materials were mostly used for waterproofing and embalming. Heavy crude oil, which is much more viscous than conventional crude oil, and tar sands, where bitumen is found mixed with sand and clay, are becoming more important as sources of fossil fuel. Oil shale and similar materials are sedimentary rocks containing kerogen, a complex mixture of high-molecular weight organic compounds, which yield synthetic crude oil when heated (pyrolyzed). These materials have yet to be exploited commercially. These fuels are employed in internal combustion engines, fossil fuel power stations and other uses.

2.1.2 Biofuel

Biofuel is defined as gas or liquid fuel that can be produced from the utilization of biomass substrates and can be serve as a (partial) substitute for fossil fuel (Giampietro et al., 1997). Biofuel produced from natural vegetable oil or fats can be used as a transportation fuel or fuel additives in the vehicle to reduce their emissions. Plant oil are attracting increased attention in this respect (Bhatia et al., 2003). Plant oils are those that are derived from plant resources such as palm oil (Tamunaidu et al., 2007)

Biofuels are fuels derived from living plants, animals or their byproducts which are not more than 20-30 years old. Biofuels contain stored solar energy and are a renewable source of energy, since the plants can be grown again. Unlike petroproducts , all biofuels are biodegradable and do not damage the environment when spilled. As demand and prices of crude oil increase, more countries are encouraging the use of biofuels by offering tax incentives.Wood from trees and manure from cattle (cow dung) are the most widely used biofuels used for cooking and other household applications in poor countries. Biogas for cooking is derived from industrial and household waste by the anaerobic digestion. Biogas contains methane. Chemical processes can also be used to produce biogas from industrial waste. Microalgae may be used as an energy source in future, as their yield per acre is the highest compared to other sources.

2.1.2 Biodiesel

Biodiesel is an alternative fuel similar to conventional or ‘fossil’ diesel. Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to Biodiesel is called transesterification. This process is described in more detail below. The largest possible source of suitable oil comes from oil crops such as rapeseed, palm or soybean. In the UK rapeseed represents the greatest potential for biodiesel production. Most biodiesel produced at present is produced from waste vegetable oil sourced from restaurants, chip shops, industrial food producers such as Birdseye etc. Though oil straight from the agricultural industry represents the greatest potential source it is not being produced commercially simply because the raw oil is too expensive. After the cost of converting it to biodiesel has been added on it is simply too expensive to compete with fossil diesel. Waste vegetable oil can often be sourced for free or sourced already treated for a small price. (The waste oil must be treated before conversion to biodiesel to remove impurities). The result is Biodiesel produced from waste vegetable oil can compete with fossil diesel. More about the cost of biodiesel and how factors such as duty play an important role can be found here.

As mentioned above biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste oils. There are three basic routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Conversion of the oil to its fatty acids and then to biodiesel.

Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield. For this reason only this process will be described in this report.

The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel productions, either base can be used for the methyl ester. A common product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol.

The figure below shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

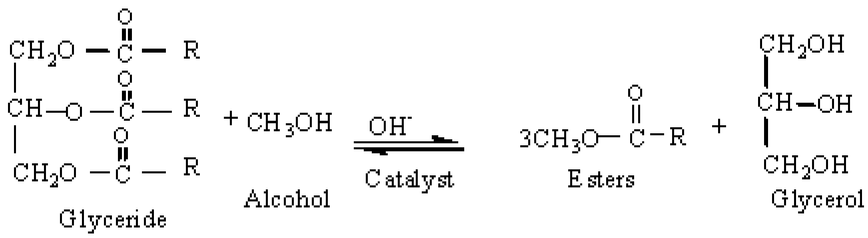

Figure 2.1: The Products of the Reaction are the Biodiesel itself and Glycerol.

2.1.4 Biopetrol from Oleic acid

Biopetrol contain isooctane as the main constituent is a fuel with high octane number through isomerisation process, has low tendency to create knocking in spark ignition engines. Oxygen in its molecule permits low-temperature combustion with reduction of CO and NOx emissions. Since that biopetrol and bioethanol both used as gasoline so its properties not vary much. Therefore biopetrol combustion also offers fuels and emission saving too. Just like other types of biofuel the advantages of biopetrol production are clarified as below:

a) Powerful solvent that will clean any engine it is run through.

b) Helps to increase the efficiency and life of engines by providing a marked improvement in lubricity which can reduce engine wear, lower engine temperature, and increase overall power.

c) Biodegradable and non-toxic.

d) Contains no sulfur and does not contribute sulfur dioxide to acid rain.

e) Helps to lower the effect of harmful emissions in our atmosphere by reducing the amount of carbon dioxide, unburned hydrocarbons, and black smoke.

Biopetrol invented today is toward global trend in manufacturing gasoline more environmental friendly but at a really great performance. Biopetrol from oleic acid research's objective is to add another kind of biofuel production beside biodiesel and bioethanol which we believe more flexible in Southeast Asia like Malaysia tropical plant. This kind of biofuel is produced from fatty acid methyl via catalytic cracking or catalytic transesterification of renewable feedstock such as oleic acid. Catalytic cracking is used as economical method to increase the conversion at a lower temperature thus saving a lot of energy beside catalyst itself can be recycled.

2.2 Petroleum Refining

Petroleum is a complex mixture of organic liquids called crude oil and natural gas, which occurs naturally in the ground and was formed millions of years ago. Crude oil varies from oilfield to oilfield in colour and composition, from a pale yellow low viscosity liquid to heavy black 'treacle' consistencies. Crude oil and natural gas are extracted from the ground, on land or under the oceans, by sinking an oil well and are then transported by pipeline and/or ship to refineries where their components are processed into refined products. Crude oil and natural gas are of little use in their raw state; their value lies in what is created from them: fuels, lubricating oils, waxes, asphalt, petrochemicals and pipeline quality natural gas.

An oil refinery is an organised and coordinated arrangement of manufacturing processes designed to produce physical and chemical changes in crude oil to convert it into everyday products like petrol, diesel, lubricating oil, fuel oil and bitumen. As crude oil comes from the well it contains a mixture of hydrocarbon compounds and relatively small quantities of other materials such as oxygen, nitrogen, sulphur, salt and water. In the refinery, most of these non - hydrocarbon substances are removed and the oil is broken down into its various components, and blended into useful products. Natural gas from the well, while principally methane, contains quantities of other hydrocarbons - ethane, propane, butane, pentane and also carbon dioxide and water. These components are separated from the methane at a gas fractionation plant.

Refinery processes have developed in response to changing market demands for certain products. With the advent of the internal combustion engine the main task of refineries became the production of petrol. The quantities of petrol available from distillation alone was insufficient to satisfy consumer demand. Refineries began to look for ways to produce more and better quality petrol. Two types of processes have been developed:

- Breaking down large, heavy hydrocarbon molecules
- Reshaping or rebuilding hydrocarbon molecules.

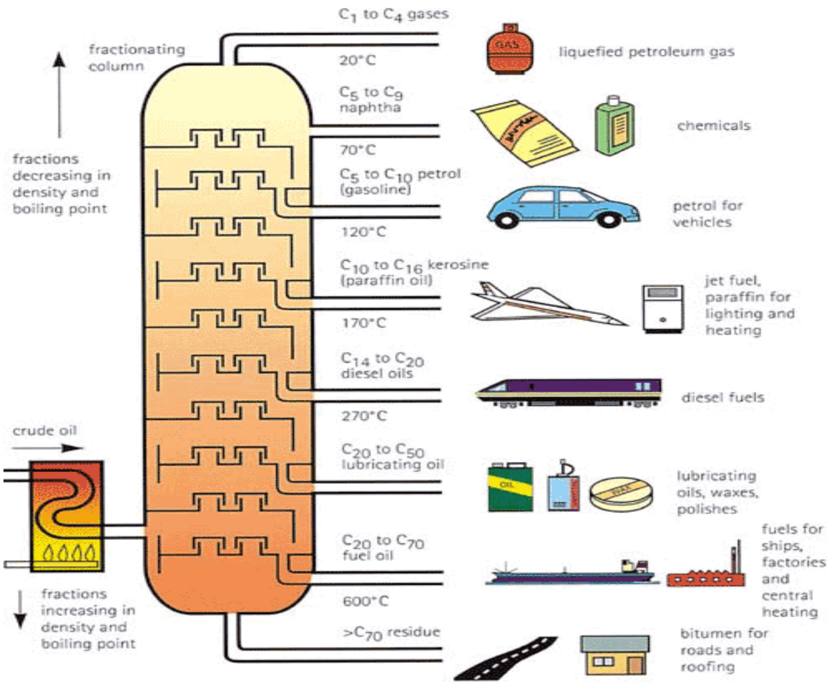

Figure2.2: Petroleum fraction of separation and its usage.

2.2.1 Gasoline

Gasoline consists of a complex mixture of hydrocarbon. Most of these are alkanes with 4-10 carbon atoms per molecule. Smaller amounts of aromatic compounds are present. Alkenes and alkynes may also be present in gasoline. Gasoline is most often produced by the fractional distillation of petroleum, also known as crude oil (it is also produced from coal and oil shale). The crude oil is separated according to different boiling points into fractions. This fractional distillation process yields approximately 250 mL of straight-run gasoline for each liter of crude oil. The yield of gasoline may be doubled by converting higher or lower boiling point fractions into hydrocarbons in the gasoline range. Two of the main processes used to perform this conversion are cracking and isomerization.

In cracking, high molecular weight fractions and catalysts are heated to the point where the carbon-carbon bonds break. Products of the reaction include alkenes and alkanes of lower molecular weight than were present in the original fraction. The alkanes from the cracking reaction are added to the straight-run gasoline to increase the gasoline yield from the crude oil. An example of a cracking reaction is: alkane

$C_{13}H_{28}$ (l) --> alkane C_8H_{18} (l) + alkene C_2H_4 (g) + alkene C_3H_6 (g)

In the isomerization process, straight chain alkanes are converted into branched chain isomers, which burn more efficiently. For example, pentane and a catalyst may react to yield 2-methylbutane and 2,2-dimethylpropane. Also, some isomerization occurs during the cracking process, which increases the gasoline quality.

2.2.2 Octane Number

Fuel octane requirements for gasoline engines vary with the compression ratio of the engine. Engine compression ratio is the relative volume of a cylinder from the bottom most position of the piston's stroke to the top most position of the piston's stroke. The higher an engine's compression ratio, the greater the amount of heat generated in the cylinder during the compression stroke.

If fuel octane is too low for a given compression ratio, the fuel prematurely and spontaneously ignites too early and the fuel charge EXPLODES rather than BURNS resulting in incomplete combustion. The net effect is a loss in power, possible engine damage, and an audible "knock" or "ping", referred to as detonation.

The octane number of gasoline is a measure of its resistance to knock. The octane number is determined by comparing the characteristics of a gasoline to isooctane (2,2,4-trimethylpentane) and heptane. Isooctane is assigned an octane number of 100. It is a highly branched compound that burns smoothly, with little knock. On the other hand, heptane, a straight chain, unbranched molecule is given an octane rating of zero because of its bad knocking properties. Straight-run gasoline (directly from the refinery distillation column) has an octane number of about 70. In other words, straight-run gasoline has the same knocking properties as a mixture of 70% isooctane and 30% heptane. Many of these compounds are straight chain alkanes. Cracking, isomerization, and other refining processes can be used to increase the octane rating of gasoline to about 90. Anti-knock agents may be added to further increase the octane rating.

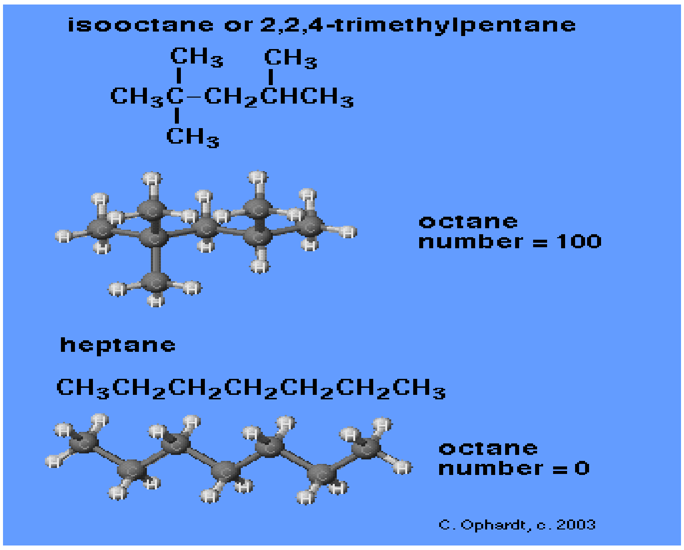

Figure 2.3: Isooctane and heptanes molecular structure

2.3 Cracking Process

Cracking is the term of breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are revaporised before cracking. Figure 2.4 shows the longer hydrocarbons broken into smaller hydrocarbons.

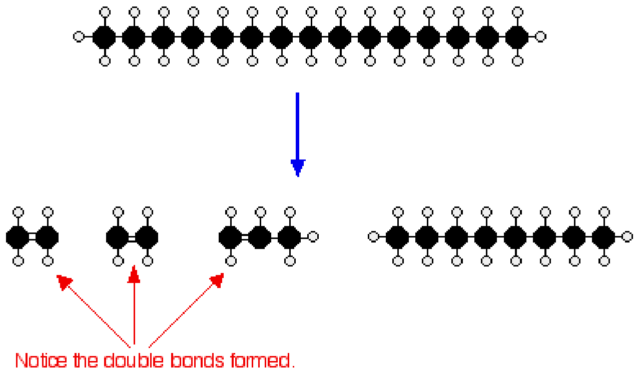

Figure 2.4: Molecules are broken into smaller hydrocarbon

This reaction involved the chain break-up for $C_{15}H_{32}$ to produce ethene, propene and octane. Ethene and propene are important materials for making plastics or producing other organic chemicals and octane is one of the molecules found in petrol (gasoline).

2.3.1 Thermal Cracking

Modern high-pressure thermal cracking operates at absolute pressures of about 7,000 kPa. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as homolytic fission and produces alkenes, which are the basis for the economically important production of polymers.